

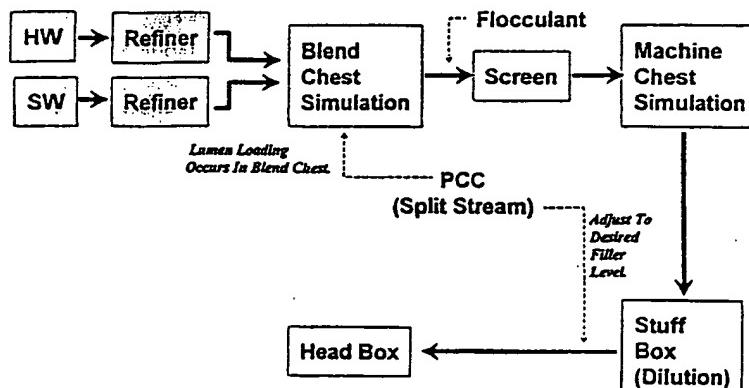


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :  D21H 17/67, 23/04		A1	(11) International Publication Number: <b>WO 98/35095</b>  (43) International Publication Date: 13 August 1998 (13.08.98)
(21) International Application Number: PCT/US98/02925 (22) International Filing Date: 10 February 1998 (10.02.98)  (30) Priority Data: 08/797,219 11 February 1997 (11.02.97) US		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(71) Applicant: MINERALS TECHNOLOGIES INC. [US/US]; 405 Lexington Avenue, New York, NY 10174-1901 (US). (72) Inventors: HOCKMAN, John, Albert; 115 North Eighteenth Street, Easton, PA 18042 (US). SOHARA, Joseph, Andrew; 3346 Delong Avenue, Bethlehem, PA 18017 (US). (74) Agents: RICHARDS, John; Ladas & Party, 26 West 61st Street, New York, NY 10023 (US) et al.		Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: LUMEN LOADING OF MINERAL FILLER INTO CELLULOSE FIBERS FOR PAPERMAKING

## LUMEN LOADING IN TYPICAL PAPERMAKING PROCESS



HW - Hardwood  
SW - Softwood

## (57) Abstract

A method of introducing and retaining particles of mineral filler inside the lumens of wood pulp fibers is disclosed. The fillers are mixed with a high-consistency pulp slurry so that a portion of the total filler diffuses inside the lumens. The loaded fiber is treated with a chemical flocculating agent that exhibits a higher chemical affinity for the filler than for the fiber. The flocculated filler particles are prevented from diffusing outside the lumens. At equal filler loading levels, paper formed according to the lumen loading process of this invention exhibits superior mechanical strength than paper prepared in a conventional manner.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KZ	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

## LUMEN LOADING OF MINERAL FILLER INTO CELLULOSE FIBERS FOR PAPERMAKING

### FIELD OF THE INVENTION

The present invention relates to mineral filled paper and a process for  
5 its preparation wherein the filler is dispersed within the lumens of the pulp fiber and  
wherein a chemical flocculant is added to the furnish, in order to bind the filler  
inside the lumens. By using the process of the present invention, the filler is  
retained within the lumens even under dilute, high shear conditions of papermaking.

### BACKGROUND OF THE INVENTION

10 Any fibrous raw material such as wood, straw, bamboo, hemp,  
bagasse, sisal, flax, cotton, jute and ramie, can be used in the manufacture of paper.  
Separation of the fibers of such materials is called pulping. The separated fibers  
which are used to make paper, are called pulp. Due to the fact that wood is  
plentiful and readily available, paper consists primarily of wood pulp fiber and  
15 insoluble particulate mineral fillers. Most fillers are considerably less expensive  
than the fibers, and as such, are added during papermaking to reduce the overall  
cost of producing the paper. Fillers are also added to the pulp fiber to impart  
certain mechanical properties such as bulk and stiffness, and optical properties such  
as brightness and opacity to the paper. Kaolin clays, chalk, talc, titanium dioxide,  
20 calcium carbonates including precipitated calcium carbonate (PCC) and ground  
calcium carbonate (GCC) are commonly used as mineral fillers in paper production.

Precipitated calcium carbonate (PCC) has been widely used as a  
preferred paper filling mineral over the last decade. The versatility of PCC has  
been one of the major catalysts for its success. For example, PCC can be prepared  
25 in a variety of particle sizes and crystal shapes or morphologies. PCC generally  
exhibits high brightness, resulting in high sheet brightness. Some PCC  
morphologies are particularly effective at increasing sheet opacity, which is  
desirable when both sides of the sheet are printed. Other PCC morphologies are  
effective in controlling the thickness (caliper) of the sheet, which is related to sheet  
30 stiffness. PCC can also affect sheet porosity, which can influence the ability of  
certain pneumatic devices to physically handle the sheet during papermaking. There  
are also other advantages in using PCC in paper production.

- 2 -

The material costs of producing paper generally decrease in direct proportion with increasing amounts of mineral filler in the filled paper. Therefore, maximizing the mineral content of paper is a major objective of the paper maker. Optical properties of the filled paper, such as brightness and opacity, also tend to 5 improve by increasing the filler content. These benefits are offset however, by a reduction in mechanical strength that generally occurs as the level of mineral filler in the sheet is increased. Paper derives its mechanical strength from bonding between adjacent pulp fibers. Fillers that are dispersed throughout the pulp fibers will disrupt the intimate contact that allows bonding between adjacent pulp fibers, to 10 occur. The greater the amount of filler in the paper, the greater will be the tendency toward disruption of fiber to fiber bonds, resulting in lower sheet strength.

Several methods have been proffered to resolve the problem of decreased sheet strength caused by increased filler loading. Some of these techniques have involved chemical modification of the filler surface using agents 15 commonly utilized as retention aids. These generally are polyelectronic synthetic polymers that act mainly through the mechanism of flocculation. Most common are polyamines and polyacrylamides.

Supplemental bonding agents are also well known as a means of improving the strength of filler loaded papers. These bonding agents can be natural 20 or synthetic polymeric substances that are added at the wet-end of a paper machine to improve the mechanical strength of the dried paper. These materials are typically starches derived from various plants such as corn, tapioca, potato and wheat, or gums derived from locust bean or guar seeds. Such gums and starches are "cooked" or otherwise prehydrated to promote swelling before they are used. Gums and 25 starches also are commonly used in papermaking as surface coatings to improve the sizing (i.e., resistance to penetration by water) of paper.

Another means of improving the strength of filled papers is through a technique called lumen loading. This involves placing the fillers directly inside the hollow spaces (i.e. lumens) of the pulp fibers. Fillers that reside inside the lumens 30 of pulp fibers do not interfere with inter-fiber bonding, and therefore have less negative impact on the mechanical strength of filled papers. Lumen loading can be accomplished through simple mechanical mixing. However, just as fillers will

- 3 -

migrate into these lumens, they can also diffuse out. Using known techniques, loading of the lumens and diffusion of the filler loaded lumens during the papermaking process, continues to be a problem for papermakers. What has been found to be novel and unanticipated by the prior art is a product and process for 5 lumen loading pulp fibers wherein a substantial level of a mineral filler can be loaded into the lumens, while paper strength reduction, is minimized.

It is therefore an object of the present invention to provide a process wherein the mineral content of paper is increased. Another object of the present invention is to reduce the cost of the papermaking process by reducing the amount 10 of pulp necessary to obtain the same quality paper by increasing the level of mineral filler. A further object of the present invention is to increase the filler content of the paper so that substantially less of the filler is lost with the drainage water, also known as "white water", during sheet formation on the paper machine. A final object is to produce a filled paper that has no deficiencies in mechanical and/or 15 optical properties.

#### RELATED ART

U.S. Pat. No. 5,223,990 discloses a method of loading cellulose fibers with calcium carbonate filler by reacting calcium hydroxide with carbon dioxide in the presence of cellulosic fibrous material.

20 U.S. Pat. No. 5,096,539 discloses a process for preparing a filled paper wherein the filler comprises an insoluble precipitate that is precipitated in situ within the cell wall of the fibers.

U.S. Pat. No. 4,510,020 discloses a process for preparing a filled paper wherein substantially all of the filler present is within the lumens of the 25 cellulosic fibers.

None of the related art references, either individually or in combination, disclose the present novel product and process for increasing the filler content of paper.

#### SUMMARY OF THE INVENTION

30 The present invention provides a process for adding a mineral filler to wood pulp fiber in a papermaking process wherein a chemical additive is used to flocculate the filler particles inside of the lumens of the fibers. The filler is

- 4 -

maintained inside the lumens of the fibers during the dilute, high shear conditions of papermaking. The present invention further provides a product having increased filler loading and acceptable optics, while physical properties such as mechanical strength are maintained.

5

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for producing filled paper by loading the lumens of the pulp fiber with a mineral filler. The filler is added to the papermaking process at a point where the concentration of the pulp is typically from about 1.0 to 5.0 weight percent. By the subsequent addition of a chemical 10 flocculant down-stream of the filler addition point, the filler is fixed and remains within the lumens during papermaking. Optionally, additional filler may be added to the papermaking process at a second addition point, in order to achieve fine control of the filler content of the final paper. By using the process of the present invention, filler is loaded within the lumens of the pulp fibers and protected from 15 drainage forces which normally cause filler dislodgement during papermaking.

According to the process of the present invention, the filler is loaded into the pulp fiber lumens by mixing or agitating the pulp fiber, the filler, and a flocculant at a point in the papermaking process when the pulp concentration is from about 1.0 to about 5.0 weight percent. Dilution of the filler/pulp fiber mixture may be necessary 20 to obtain the desired furnish consistency of usually from about 0.3 to about 1.0 percent, preferably about 0.5 percent, prior to delivery to the paper machine.

An integral aspect of the process of the present invention is the structure of the papermaking fiber. The strength of paper is highly dependent upon the fibers of the pulp, used to make paper, becoming bonded extensively to one 25 another during papermaking. The most widely used fibers are those derived from wood and, as liberated by pulping, the majority appear under the microscope as long hollow tubes, uniform in size for most of the length but tapered at each end. Along the length of the fiber, the fiber wall is perforated by small apertures(pits) which connect the central cavity(lumen) to the fiber exterior. The process for placing 30 mineral fillers within the lumens is called lumen loading and is applicable to a wide range of papermaking fibers.

The present process can be carried out on fibers derived from many

- 5 -

- species of wood, by any of the common pulping and bleaching procedures. The fiber may be hardwood fiber, softwood fiber or a mixture of both hard and soft wood fibers. However, in order to realize maximum loading of the lumens with filler, the pulp fiber should enter the process of the present invention in
- 5 "never-dried" form. Drying the pulp fiber irreversibly collapses a large portion of the lumens and renders them inaccessible to the mineral filler. Reslurrying of dried pulp fiber is less susceptible to the full benefit of the novel process for lumen loading of the present invention, but having full knowledge of this limitation, may be used.

10           The concentration or consistency of the pulp fiber slurry is preferably in the range of from about one percent to about five percent, based on the total weight of the slurry. In a preferred embodiment of the invention, the consistency of the pulp fiber slurry is preferably in the range of from about two percent to about four percent, based on the total weight of the slurry.

15           Kaolin clays, chalk, talc, titanium dioxide, alumina, silica, precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) are commonly used as mineral fillers in paper production. A filler consists of fine particles of an insoluble solid, usually of a mineral origin. By virtue of the high surface area and sometimes high refractive index, fillers confer improved optical properties such as opacity and brightness to the paper. Enhancement of the optical properties of the mineral filled paper is a principal objective in adding fillers to the paper furnish, although other advantages, such as improved smoothness, improved printability and improved durability, can be imparted to the paper.

20           Although kaolin clays, chalk talc, titanium dioxide, alumina, silica, PCC, GCC and the like, may be used in the process of the present invention, the preferred filler is precipitated calcium carbonate (PCC). The PCC has an average particle size in the range from about 0.5 to about 2.0 microns( $\mu\text{m}$ ). In a preferred embodiment of the present invention, the average size of the PCC is in the range of from about 0.7  $\mu\text{m}$  to about 1.4  $\mu\text{m}$ . The PCC morphology may be orthorhombic, rhombic or scalenohedral. Other fillers, such as ultrafine ground limestone (UFLG) also may be used in the process of the present invention.

25           According to one embodiment of the present invention, an aqueous

- 6 -

slurry of mineral filler is mixed, by any known mechanical means, into an aqueous slurry of wood pulp fiber. For loading of the lumens, the pulp may be in a never-dried state, in order to obtain the maximum loading benefit. The filler is added to the pulp as an aqueous slurry, so that the filler solids, after mixing with 5 the pulp fiber, represent from about 5 weight percent to about 80 weight percent based on the total solids. In a preferred embodiment of the invention, the filler solids represents from about 20 weight percent to about 40 weight percent based on the total solids.

The filler and fiber components are mixed under agitation for a 10 period of time to allow maximum loading of the lumens. It has been found that a minimum of five minutes of agitation is necessary to obtain maximum loading. Shorter mixing times do not provide maximum lumen loading benefits. In a preferred embodiment of the present invention, the period of mixing or agitation can range from about 10 minutes to about 30 minutes. There is no known upper limit 15 on the time of mixing, outside of that imposed by practicality and economics. During the time that the fiber and filler components are mixed together, some of the filler becomes dispersed within the fiber lumens. This occurs by mechanical diffusion.

Certain factors strongly influence the level of filler that can be 20 practically loaded into the fiber lumens. One such factor is the average particle size of the mineral filler. Fillers having smaller average particle sizes will more easily diffuse into the lumens than larger particle size fillers. In addition, the relative concentrations of fiber and filler that are present when the two components are mixed, will also determine the extent to which lumen loading occurs. Finally, the 25 period of time the filler and fiber components are mixed, influence how much lumen loading will occur in the paper furnish.

According to the present invention, the amount of filler that diffuses into the lumens, typically is from about 0.5 percent to about 10 percent of the combined weight of fiber and filler. In a preferred embodiment of the invention 30 from about 3 percent to about 6 percent of the total weight of fiber and filler is lumen loaded filler.

Another integral aspect of the process of lumen loading of the present

- 7 -

invention requires that a flocculating chemical be added to the pulp fiber-filler mixture, after the pulp fiber-filler components have been sufficiently mixed. The use of such a flocculant causes any filler that resides within the fiber lumens to form agglomerates of sufficient size to prevent diffusion outside the lumens during 5 paper production. This also causes filler outside the lumens to also form agglomerates. The formation of agglomerates reduces the tendency of filler particles to interfere with inter-fiber bonding, fixes and holds the filler inside and outside the lumens, thus preventing dislodgement of the filler during papermaking.

The flocculating chemical may be selected from that group of 10 materials that are polymers of glucose derived from plants, called starches. Plants from which starches are principally obtained are corn, tapioca, potato and wheat. Before it is used as a chemical flocculant in the present product, the starch is "cooked", in a manner consistent with the manufacturer's recommendation, to promote dissolution and swelling. This is an important aspect of the present 15 invention since the formation of agglomerates both inside the lumens and outside of the lumens result in maximum lumen loading.

Starches may be used as they naturally occur, or they may be 20 chemically modified using various techniques. Chemical modification may render the starch cationic, anionic or amphoteric. In the production of the product and according to the process of the present invention, the starch is preferably an amphoteric waxy corn starch.

Other chemical agents may also be used to flocculate the lumen 25 loaded filler. The flocculating agent is selected from those materials that exhibit a stronger chemical affinity for PCC than for wood pulp fiber. The chemical affinity is measured using the technique of batch calorimetry. When a chemical agent is brought into contact with the mineral surface, adsorption of the chemical agent will occur at the mineral surface only if sufficient affinity exists between the two materials. Adsorption is an exothermic process that liberates heat. Adsorption also can occur for a chemical agent that is brought into contact with wood pulp fibers. 30 The magnitude of the interaction between a flocculating agent and the mineral filler is measured to determine which provides maximum benefit. A separate measurement is made to determine the magnitude of the interaction between the

- 8 -

flocculating agent and a microcrystalline cellulose that is chemically similar to wood pulp.

In a preferred embodiment of the current invention, the magnitude of the flocculant-mineral interaction, expressed in calories, is at least equal to the  
5 magnitude of the flocculant-cellulose interaction for equal proportions of materials. More preferably, the magnitude of the flocculant-mineral interaction is at least 50 percent greater than the interaction between flocculant and cellulose. Most preferably, the magnitude of the flocculant-cellulose interaction is zero (0). The current invention is advantageous over other lumen loading techniques in that it  
10 offers a means of preventing diffusion of filler particles outside the fiber lumens without the need for a drying step. This results in a reduction in energy cost and an increase margin of profit for the papermaker.

In another embodiment of the invention, the filler and the flocculating chemical are slurried and first mixed, preferably, from about 10 to about 30 minutes, and then this mixture is added to the aqueous slurry of wood pulp fiber.  
15

Figure I demonstrates an aspect of how the process of the present invention could be used in a typical papermaking process. The filler addition is split such that filler may be added to the furnish at the blend chest and again at the head box. Between these two addition points, but after the first addition point, a  
20 chemical flocculant is added to the pre-mixed fiber-filler components in order to fix or hold the filler where it resides inside and outside of the fiber lumens.

The following examples are presented to further illustrate the novel process and novel product of the present invention. They should be viewed as non-limiting illustrations of the present invention and should, under no instances, be  
25 used to limit the scope of the present invention, except as presented in the appended claims.

#### EXAMPLES

In the following examples, one or more processes are described which involve addition of a mineral filler to a high-consistency slurry of wood pulp  
30 fiber. After the filler and fiber are mixed, a flocculating chemical is added so that filler particles that have diffused into the fiber lumens are agglomerated and prevented from diffusing outside the lumens. The flocculating agent is selected

- 9 -

from those chemicals that exhibit greater chemical affinity for the filler than for cellulose fiber. Chemical affinity is quantified using the technique of batch calorimetry. Alternately, the mineral filler and flocculating chemical are mixed and then added to a high consistency slurry of wood pulp fiber slurry. The resulting  
5 mixture is formed into paper exhibiting good mechanical strength at high filler loading levels.

Example 1

Into a 4-liter glass reactor was placed 200 milliliters (ml) of 4 weight percent consistency (solids) never-dried hardwood pulp. The pulp was mixed at 300 rpm with a large flat blade such that a gentle churning action occurs. Scalenohedral calcium carbonate slurry having 20 weight percent solids content was added to the mixing hardwood pulp in such an amount that the dry calcium carbonate content represented 40 weight percent of the total solids of the mixture. The calcium carbonate/pulp aqueous slurry was stirred for an additional 30 minutes. An  
15 amphoteric waxy corn starch (CATO 225 from National Starch Corporation) which was cooked at 200°F. for 30 minutes at 1 weight percent solids was added to the calcium carbonate/pulp aqueous slurry. The quantity of starch corresponds to a 4.0 weight percent on a dry calcium carbonate basis. The calcium carbonate/pulp/starch aqueous slurry was stirred for 30 minutes. The mixture was made into a paper  
20 sheet on a stainless steel wire using a Formax unit. The basis weight of the sheet approximates 170 grams per meter square ( $\text{g}/\text{m}^2$ ). The sheet was pressed between felts at 25 psi and dried on a drum drier at 265°C. These dried sheets represent the commercial hardwood dry lap containing calcium carbonate, which was combined with softwood dry lap in the desired proportions. The percent calcium carbonate of  
25 the hardwood dry lap is measured so as to definitively determine the amount of dry hardwood present. The hardwood containing sheets were refined by combining 360 grams hardwood (from the hardwood dry lap) and 24 liters of water and stirring the mixture in a Valley Beater to 360 Canadian Standard Freeness (CSF). A mixture was prepared by combining 360 grams of untreated softwood pulp and 24 liters of  
30 water. The mixture was refined by mixing in a Valley Beater to 400 CSF. The refined hardwood and the refined softwood were combined such that a 60 percent hardwood/40 percent softwood mixture results. Water was added to the mixture to

- 10 -

adjust the solids to 0.3 weight percent on a dry pulp basis.

Handsheets were prepared ( $60 \text{ g/m}^2$ ) using a Formax Sheet Former (Noble and Wood type, from Adirondack Machine Corp) from a furnish of 60 percent hardwood (containing calcium carbonate in the lumen) and 40 percent bleached softwood pulps beaten to 400 CFS at pH 7 in distilled water. The pulp consistency was 0.3 percent. A retention aid (high molecular weight cationic polyacrylamide) Percol® from Allied Colloids was added to the pulp furnish in an amount equal to 0.05 percent (1lb./ton of paper). Synthetic sizing agent (alkyl ketene dimer) was added to the pulp furnish at a level of 0.25 percent (5lbs./ton of paper). The mixture was made into a paper sheet on a stainless steel wire using a Formax unit. The sheet was pressed between felts at 25p.s.i. and dried on a drum dryer at  $265^\circ\text{C}$ . The sheets were conditioned at 50 percent relative humidity and  $23^\circ\text{C}$ . prior to testing.

The paper strength was determined by testing the breaking length (TAPPI test method T-494 OM-88) and the Scott Bond (TAPPI test method UM 403). The paper brightness was measured according to TAPPI test method T452-OM92 and the paper opacity was measured according to TAPPI test method T425-OM-91 (corrected to  $60.5 \text{ grams/m}^2$  basis weight).

The strength of the paper, using as filler the lumen containing calcium carbonate in accordance with the present invention, is greater than that of the control paper (not lumen loaded, but having an equivalent amount of filler added in the conventional manner).

	CONTROL (Not Lumen Loaded)	PRESENT INVENTION (Lumen Loaded)
Weight Filler (Percent)	24	24
25      Breaking Length (Meters)	2127	3128
Scott Bond (Foot lbs in Thousandths)	34.2	53.6
TAPPI Brightness (Percent)	89.3	89
TAPPI Opacity (Percent)	87.6	87.6

- 11 -

Example 2

A mixture of 270 grams of hardwood pulp and 90 grams of softwood pulp (75 percent hardwood/25 percent softwood) was combined with 24 liters of water and refined in a Valley Beater to 400 CSF. The pulp consistency was 1.5 percent. Water was removed by screening the pulp through a 100 mesh screen to raise the consistency of the pulp to 3.8 percent. The pulp fine water was set aside for later use. The 3.8 percent consistency was used to simulate the solids of pulp in an integrated mill. An integrated paper mill is one that prepares its own pulp as opposed to acquiring pulp from the open market.

10        Into a 4-liter glass reactor was placed 1000 ml of the previously described 3.8 percent consistency pulp. The pulp was mixed at 100 rpm with a large flat blade such that a gentle churning action occurred. Scalenohedral calcium carbonate slurry at 20 weight percent solids was added to the mixing hardwood/softwood pulp in such an amount that the dry calcium carbonate represented 15 weight percent of the total solids of the mixture. The calcium carbonate/pulp aqueous slurry was stirred 10 minutes. A cationic potato starch (STA-LOK® 400 from A.E. Staley Manufacturing Company) which was cooked at 200°F. for 30 minutes at 1 percent solids was added to the calcium carbonate/pulp aqueous slurry. The quantity of starch corresponds to 4.0 weight percent on a dry calcium carbonate basis. The calcium carbonate/pulp/starch aqueous slurry was then stirred for 10 minutes. The mixture was then diluted with 1622 ml of the pulp fine water so as to re-introduce all fines that were removed during the screening process. The mixture was further diluted with 9500 ml water to adjust the final consistency to approximately 0.3 percent.

25        Paper handsheets were then prepared from the above-described hardwood/softwood pulp containing the calcium carbonate and hardwood/softwood pulp containing no calcium carbonate loaded in the lumen. The handsheets were prepared and tested as described in Example 1. Hercules Size Test (HST) was used to measure the penetration of liquid through the handsheets. The test was performed on a Hercules Sizing Tester Model KA or KC and the test method employed is TAPPI Test Method T-530 PM-89 (Revised 1989).

The paper strength, i.e. Breaking Length and Scott Bond of the paper,

- 12 -

which contains the calcium carbonate loaded lumen in accordance with the present invention is greater than that of the control paper (not lumen loaded). The paper which contains the calcium carbonate loaded lumen also exhibits improved sizing.

	CONTROL (Not Lumen Loaded)	PRESENT INVENTION (Lumen Loaded)
5    Weight Filler (Percent)	16	16
Breaking Length (Meters)	2970	3350
Scott Bond (Foot lbs in Thousandths)	49.2	58.2
HST Sizing (Percent)	23	103
TAPPI Opacity (Percent)	88.1	88.2
10    TAPPI Opacity (Percent)	87.5	88

- 13 -

C L A I M S

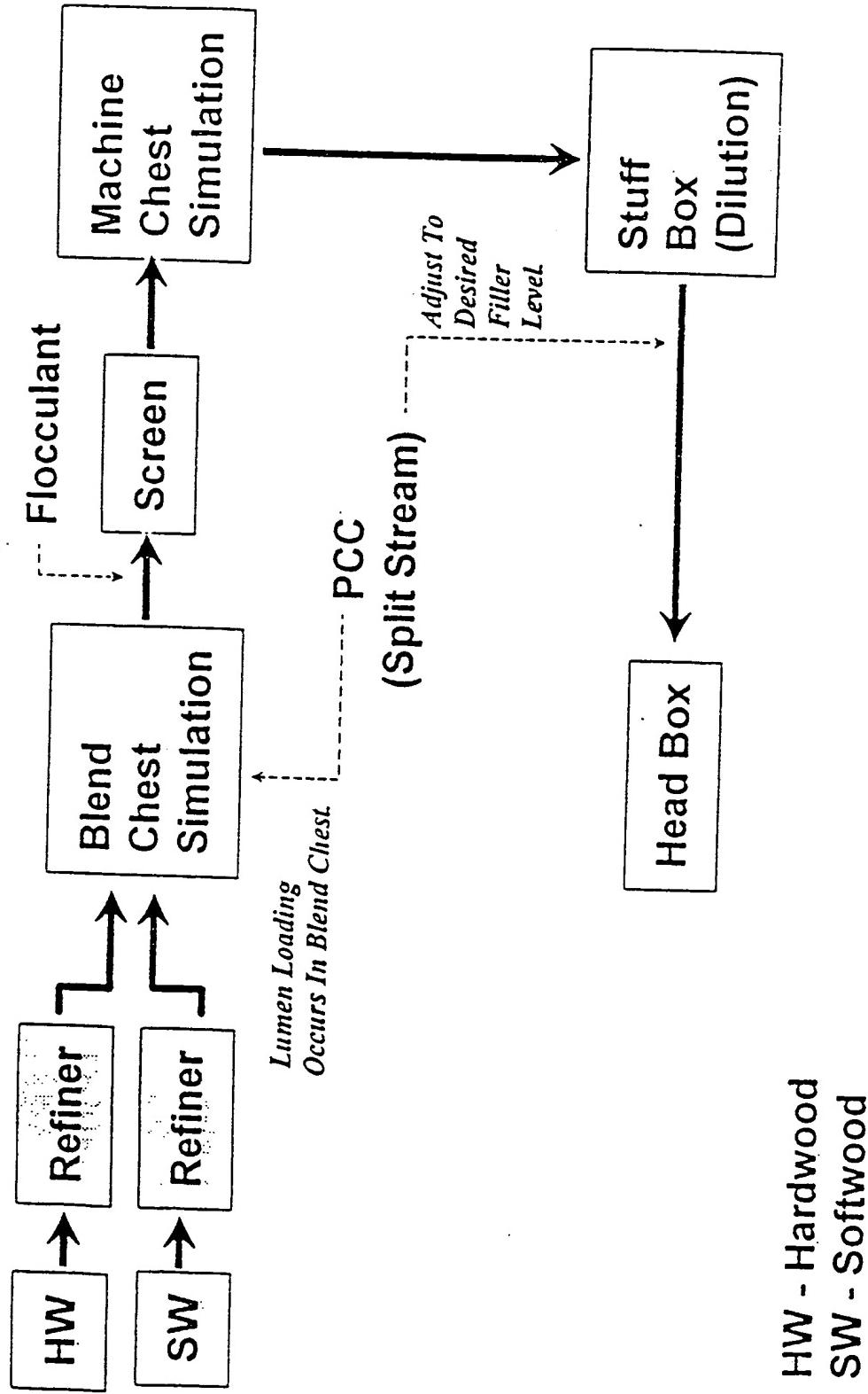
1. A process for producing a mineral filled paper which comprises mixing an aqueous slurry of mineral filler with a aqueous slurry of wood pulp fiber and adding a chemical flocculant in a papermaking furnish to produce paper having a substantial amount of filler inside the lumens of the cellulose fibers.
- 5 2. The process as claimed in claim 1, wherein the furnish is substantially diluted to from about 0.3 weight percent to about 1.0 weight percent.
3. The process as claimed in claim 1 or 2, wherein the mineral filler is calcium carbonate.
- 10 4. The process as claimed in claim 3, wherein the calcium carbonate is precipitated calcium carbonate.
5. The process as claimed in any one of the preceding claims, wherein the concentration of the wood pulp fiber is from about 1.0 weight percent to about 5.0 weight percent, based on the total weight of the slurry.
- 15 6. The process as claimed in claim 5, wherein the concentration of the wood pulp fiber is from about 2.0 weight percent to about 4.0 weight percent, based on the total weight of slurry.
7. The process as claimed in any one of the preceding claims, wherein said mineral filler is precipitated calcium carbonate having an average particle size 20 of from about 0.5 microns to about 2.0 microns.
8. The process as claimed in claim 7, wherein the average particle size of the precipitated calcium carbonate is from about 0.7 microns to about 1.4 microns.
9. The process as claimed in any of the preceding claims, wherein said 25 mineral filler is calcium carbonate and said calcium carbonate represents from about 5 weight percent to about 80 weight percent of the total solids of the furnish.
10. The process as claimed in any of the preceding claims, wherein said mineral filler is calcium carbonate and said calcium carbonate represents from about 20 weight percent to about 40 weight percent of the total solids of the furnish.
- 30 11. The process as claimed in any of the preceding claims, wherein the aqueous slurry of mineral filler and the aqueous slurry of fiber are mixed for from about 10 to about 30 minutes.

- 14 -

12. The process as claimed in any of the preceding claims, wherein the flocculating chemical is selected from the group of starches consisting of corn, tapioca, potato, and wheat.
13. The process as claimed in any of the preceding claims, wherein the flocculating agent is cationic, anionic or amphoteric starch.
14. The process of claim 13, wherein the starch is amphoteric waxy corn starch.
15. The process according to claim 1, wherein the aqueous slurry of mineral filler and chemical flocculant are first combined and mixed prior to combining with the aqueous slurry of wood pulp fiber in a papermaking furnish.
16. A mineral filled paper wherein the weight of filler inside the lumens is from about 0.5 weight percent to about 10 weight percent filler, based on the total weight of fiber and filler.
17. A mineral filled paper wherein the weight of filler inside the lumens is from about 3.0 weight percent to about 6.0 weight percent based on the total weight of fiber and filler.

1/1

**FIGURE 1 - LUMEN LOADING IN TYPICAL PAPERMAKING PROCESS**



# INTERNATIONAL SEARCH REPORT

I National Application No  
PCT/US 98/02925

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 D21H17/67 D21H23/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHANG, S. ET AL: "Lumen Loading with Calcium Carbonate Pigments" TAGA PROCEEDINGS 1997 (TAGA), SESSION: EXPERIMENTAL ANALYSIS OF PRINTING: 639-657 (1997;TAGA). 'ENGL.!', XP002065927 see page 643, paragraph 1-2 see page 647, paragraph 1-3 ----- X DATABASE PAPERCHEM THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US KIM, S. H. ET AL: "Effect of Lumen Loading on Paper Properties of Pulp Fiber" XP002064536 see abstract & J. TAPPIK 25, NO. 2: 31-41 (1993). 'KOREAN;ENGL. SUM.!', ----- -----	1-3,7-9, 11,16,17  1,15
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

26 May 1998

16/06/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Songy, O

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/02925

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 510 020 A (GREEN HAROLD V ET AL) 9 April 1985 cited in the application see the whole document -----	1-17
A	US 5 096 539 A (ALLAN G GRAHAM) 17 March 1992 cited in the application see the whole document -----	1-17

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 98/02925

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 4510020	A 09-04-1985	CA	1152266 A		23-08-1983
		EP	0042234 A		23-12-1981
		FI	811806 A, B,		13-12-1981
		JP	1652131 C		30-03-1992
		JP	3016434 B		05-03-1991
		JP	57061799 A		14-04-1982
US 5096539	A 17-03-1992	AT	111988 T		15-10-1994
		AU	6141790 A		22-02-1991
		CA	2063567 A		25-01-1991
		DE	69012821 D		27-10-1994
		DE	69012821 T		16-02-1995
		EP	0484398 A		13-05-1992
		FI	100196 B		15-10-1997
		JP	3152295 A		28-06-1991
		NO	177542 B		26-06-1995
		WO	9101409 A		07-02-1991

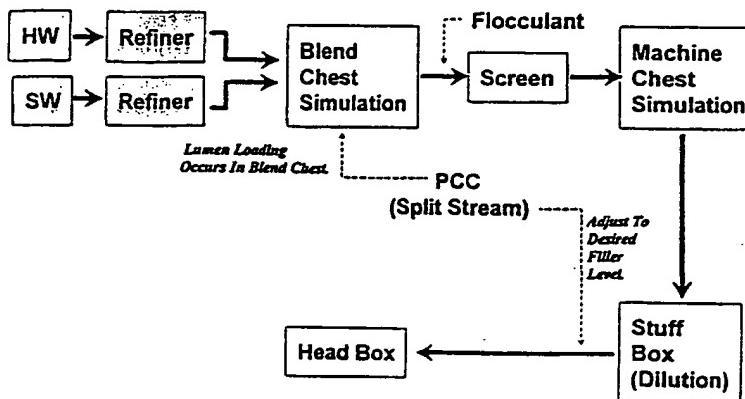


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :	A1	(11) International Publication Number: WO 98/35095
D21H 17/67, 23/04		(43) International Publication Date: 13 August 1998 (13.08.98)
<p>(21) International Application Number: PCT/US98/02925</p> <p>(22) International Filing Date: 10 February 1998 (10.02.98)</p> <p>(30) Priority Data: 08/797,219 11 February 1997 (11.02.97) US</p> <p>(71) Applicant: MINERALS TECHNOLOGIES INC. [US/US]; 405 Lexington Avenue, New York, NY 10174-1901 (US).</p> <p>(72) Inventors: HOCKMAN, John, Albert; 115 North Eighteenth Street, Easton, PA 18042 (US). SOHARA, Joseph, Andrew; 3346 Delong Avenue, Bethlehem, PA 18017 (US).</p> <p>(74) Agents: RICHARDS, John; Ladas &amp; Parry, 26 West 61st Street, New York, NY 10023 (US) et al.</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With a revised version of the international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> <p>(88) Date of publication of the revised version of the international search report: 29 October 1998 (29.10.98)</p>

(54) Title: LUMEN LOADING OF MINERAL FILLER INTO CELLULOSE FIBERS FOR PAPERMAKING

LUMEN LOADING IN TYPICAL  
PAPERMAKING PROCESS



HW - Hardwood  
SW - Softwood

(57) Abstract

A method of introducing and retaining particles of mineral filler inside the lumens of wood pulp fibers is disclosed. The fillers are mixed with a high-consistency pulp slurry so that a portion of the total filler diffuses inside the lumens. The loaded fiber is treated with a chemical flocculating agent that exhibits a higher chemical affinity for the filler than for the fiber. The flocculated filler particles are prevented from diffusing outside the lumens. At equal filler loading levels, paper formed according to the lumen loading process of this invention exhibits superior mechanical strength than paper prepared in a conventional manner.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republie of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 D21H17/67 D21H23/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	CHANG, S. ET AL: "Lumen Loading with Calcium Carbonate Pigments" TAGA PROCEEDINGS 1997 (TAGA), SESSION: EXPERIMENTAL ANALYSIS OF PRINTING: 639-657 (1997;TAGA). [ENGL.], October 1997, XP002065927 see page 643, paragraph 1-2 see page 647, paragraph 1-3 --- X DATABASE PAPERCHEM THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US KIM, S. H. ET AL: "Effect of Lumen Loading on Paper Properties of Pulp Fiber" XP002064536 see abstract & J. TAPPIK 25, NO. 2: 31-41 (1993). [KOREAN;ENGL. SUM.], --- -/-/	1-3,7-9, 11,16,17  1,15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

24 August 1998

Date of mailing of the international search report

01 09. 1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Songy, 0

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 98/02925

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 510 020 A (GREEN HAROLD V ET AL) 9 April 1985 cited in the application see the whole document -----	1-17
A	US 5 096 539 A (ALLAN G GRAHAM) 17 March 1992 cited in the application see the whole document -----	1-17

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 98/02925

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4510020	A 09-04-1985	CA 1152266 A		23-08-1983
		EP 0042234 A		23-12-1981
		FI 811806 A, B,		13-12-1981
		JP 1652131 C		30-03-1992
		JP 3016434 B		05-03-1991
		JP 57061799 A		14-04-1982
US 5096539	A 17-03-1992	AT 111988 T		15-10-1994
		AU 6141790 A		22-02-1991
		CA 2063567 A		25-01-1991
		DE 69012821 D		27-10-1994
		DE 69012821 T		16-02-1995
		EP 0484398 A		13-05-1992
		FI 100196 B		15-10-1997
		JP 3152295 A		28-06-1991
		NO 177542 B		26-06-1995
		WO 9101409 A		07-02-1991